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Lattice phonon mediation of solid state photoreactions in organic crystals

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Abstract : Physical or chemical change in a crystal lattice manifests itself as a change in its phonon spectrum. Laser Raman spectroscopic technique is being successfully used to study crystalline state photoreactions in organic materials. The main thrust of such study has been to investigate the role of phonons in such reactions.

Electronic spectroscopy has generally been used to determine the extent of reaction progress and also to determine the nature of the photoprocesses involved. Infrared and Raman spectroscopy have been used to characterize the reactants and the products. Raman phonon spectroscopic study has been used to investigate whether the reaction occurs by homogeneous mechanism where the product form solid solution in the reactant lattice or by heterogeneous mechanism where the reactant and the product form separate lattices.

Phonon participation in such reactions are shown to occur through strong exciton phonon coupling or through a mode softening. In some reactions, however lattice phonons do not influence reactivity and topochemical control is sufficient to explain crystalline state reactivity.

Keywords : Laser Raman spectroscopy, solid state photoreaction, exciton-phonon coupling, phonon mode softening

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Plan of the article

1. Introduction

The reactivity of organic materials in the crystalline state when photoirradiated, depends on molecular packing arrangement in the lattice. This requires special attention to the role of phonons in such reactivity. The study of phonons provide information about the dynamic aspects of such reactions. In this essentially experiment oriented article phonon participation in solid state photoreaction is discussed. The discussion on the theoretical background is kept limited but sufficient to be useful for understanding of the process.

The research on solid state photoreactions has gained appreciable attention only after the pioneering work of Schmidt and his co-workers [1,2] who investigated the role of molecular packing in solid state reactions. According to Schmidt the reactivity and molecular structures of the products depend on separation distance and mutual orientation of potentially reactive functional groups. This led to what is known as "topochemical principle". According to this principle the centre to centre distance between the reactive groups is to be less than 4.2 A for the reaction to occur. However, this upper limit is not very restrictive because of nonavailability of data in the range 4.2 – 4.7 Å [3]. The another criterion is the parallelism of reactive double bonds

Indeed in many cases such as trans cinnamic acids, benzoquinones, thymine, α- benzylidine–γ–butyrolactone, 2–benzyl–5–benzylidene clyclopentanone, 3–methyl–4–nitro 5–styrylisoxazole and many other compounds the potentially reactive groups are separated by a critical distance and the reacting double bonds are parallel. Photodimerization of 2–benzyl 5–benzylidene cyclopentanone and photopolymerization of diacetylene deserves special mention. In these cases structural perfection is very much similar to that of monomer crystal and the reactant and product form solid solution over the entire conversion range [4].

In a large number of solid state photoreactions apparent violation of topochemical principle is also observed. In *p*–formyl cinnamic acid, a 100% yield of dimer is obtained although the double bonds have center–center distance greater than 4.8A [5]. Some reactions have been reported where reacting double bonds are nonparallel [6,7,8]. In 7–methoxy

coumarin reactive double bonds are rotated with respect to one another by 65° [9]. Again in 2-benzylidene cyclopentanone though the reacting double bonds are at a distance less than 4.2 A, no photoreaction occurs on prolonged irradiation [10]. These results suggest that topochemical principle is insufficient to account for many solid state reactions. The motion of phonons plays an important role in the photoreactions in these crystals. Attempts have been made to explain solid state photoreactivity by considering the orbital overlap rather than parallel double bond separation [10,11].

2. Theoretical background

A Phonon–delocalisation and relaxation :

Phonon modes originate due to rotational and translational oscillations of the molecules in the lattice. In organic crystals lattice vibrational frequencies are well separated from the internal molecular modes due to the fact that in such crystals the intermolecular forces are 10–100 times weaker than the intramolecular forces. The lattice vibrational frequencies in the organic crystals generally lie below 200 cm^{-1}. Internal vibrations are generally at higher frequency, though some out of plane deformation and torsional modes are also active in the low frequency domain. As any physical change alters the phonon spectrum, solid state phase separation or the change due to solid state photoreaction can conveniently be studied by phonon spectroscopic method. In order to characterize the nature of phonon motions in organic crystals two aspects are studied : (i) delocalization of phonons and (ii) relaxation of phonons.

(i) Delocalization .

In a real crystal with impurities or in a mixed crystal the phonon frequency is no longer precisely defined as in a pure crystal.

If the difference between the phonon frequency of host pure crystal and impurity pure crystal is smaller than the phonon band width of the host, amalgamation of phonon results [12–15]. In this limit the phonon frequencies show a monotonic shift with increasing impurity concentration. The reaction mechanism in the solid state is said to be homogeneous when the product form solid solution with the reactant in the molecular level. Such a mechanism has been suggested for solid state photopolymerization of several diacetylenes [16–18].

When the perturbation caused by the impurity is large, localised impurity bands also appear along with pure host bands. The impurity modes may be localised high frequency modes, gap modes or pseudo localised modes [19,20]. In solid-state photoreaction this situation gives segregated phonon spectra and the reaction mechanism is said to be heterogeneous. Such mechanism has been established for solid state photopolymerization of 1,4 bis [β-pyridyl (2) vinyl] benzene [21].

In some cases reaction mechanism is homogeneous in the initial stages and becomes heterogeneous as product concentration increases [22,23].

The theory is based mainly on the work of Elliott *et al* [24]. They have used Green's function to solve the problem.

For a pure host crystal, Green's function G is found to satisfy the following matrix equation

$$G^0(\omega^2) = \left[M^0\omega^2 - \phi^0\right]^{-1}, \tag{1}$$

where M^0 is the mass coefficient and ϕ^0 is the force constant for the pure crystal and the Green's function is defined as

$$G_{\alpha\alpha'}(l,l',t) = \langle\langle u_\alpha(l,t), u_{\alpha'}(l',0)\rangle\rangle \\ \frac{2\pi}{i\hbar}\,\theta(t-t')\,\langle[u_\alpha(l,t), u_{\alpha'}(l',0)]_T\rangle . \tag{2}$$

Where $\theta(t - t')$ is the Heaviside unit step function. Hence, introducing the perturbation matrix $V(\omega)$ due to both mass and force constant change

$$V(\omega) = \left(M^0 - M\right)\omega^2 + \left(\phi - \phi^0\right), \tag{3}$$

we obtain Dyson equation

$$G = G^0 + G^0VG , \tag{4}$$

which may be expanded as a power series

$$G = G^0 + G^0VG^0 + G^0VG^0VG^0 + \cdots \tag{5}$$

This expansion is trivially summed exactly to give

$$G = G^0 + G^0TG^0 , \tag{6}$$

where T matrix is defined by

$$T = V\,(I - G^0V)^{-1} . \tag{7}$$

Where I is the unit matrix.

In the amalgamation limit, the poles of G corresponds to the poles of G^0, shifted in frequency. On the other hand there will be new poles of G^0 where T has poles and these will be the new bands due to impurity.

Green's function can be calculated using different approximation methods based on configurational averaging. Configurationally averaged $\langle G \rangle$ can be represented as

$$\langle G \rangle = G^0 + G^0\Sigma\langle G \rangle , \tag{8}$$

where Σ is the self energy.

There are mainly three approximation methods for obtaining the appropriate Green's function :

(i) Virtual crystal approximation : This was first used in electronic problem by Nordheim [25]. This approximation is applied when the perturbations *i.e* mass and force constant change is small. Here the frequencies of the phonon bands in the mixed crystal shift linearly with concentration. This is just a special case of amalgamation limit. (ii) Average T matrix approximation : This is applied when the perturbation is large and localized states appear [26–30]. Here, the self energy is localised and the complex has a pole near the pole of T matrix. The poles of T matrix give the localized phonons of the impurity. According to this approximation, the frequencies are shifted by an amount Re (Σ) and broadened by Im (Σ). (iii) Coherent potential approximation : Klander [31] and Davies and Langer [32] were the first to treat the single site scattering with a self consistent field. Afterwards, Taylor [33] and Stoven [34] applied it to phonon and electronic problems respectively. The important feature of this approximation is its invariance with respect to the choice of host lattice and its correct limiting values.

(ii) Relaxation .

The study of anharmonicity of vibration in crystal reveals important temperature effect and already a number of 'soft' modes of vibrations whose frequencies depend upon temperature have been found in connection with phase transition study. In most of the order–order transitions, the structural distortions are characterised by an unstable or soft mode whose frequency goes towards zero value as the temperature approaches the phase transition temperature. The soft modes are usually damped. Structural phase transitions are generally accompanied by large amplitude displacement since the restoring force which opposes displacement goes to zero as the mode softens. In solid state photoreactions this large amplitude displacement can bring the molecules in favourable configuration for the reaction to occur. Apart from different phase transition studies thermal rearrangement reaction of methyl–*p*–amino benzene sulphonate [35], non-thermal B - A conformation change in DNA double helix [36], solid state photoreactions in ortho-methoxy trans cinnamic acid [37] and 7 -methoxy coumarin [38] are the cases where mode softening is observed.

Eyster and Prohofsky [36] have used the nonbonded interaction model to deduce the theory of non-thermal mode softening. In this model, it is assumed that there is no change in the strong chemical bonds.

The nonbonded interaction terms can be written as the sum of pair interactions between every pair of atoms not bonded to each other by stronger bonds.

The total potential energy for the solvent free case, is given by

$$V_{nb} = \sum_{n} \sum_{m} \sum_{i,j} (V_1 + V_2), \tag{9}$$

where V_1 is the familiar van der Waals 6 -- 12 function and V_2 is the electrostatic term. i and j are indices of atoms in repeat units n and m respectively.

Expanding about equilibrium position, we obtain

$$V_{nb} = \frac{1}{2} \sum_{n} \sum_{m} q_{nm}^{T} f^{nm} q_{nm} \tag{10}$$

where f^{nm} is a square diagonal matrix of harmonic force constants of dimension N^2 and q_{nm} is a column vector of dimension N^2 whose elements are small changes in the nonbonded distances. The nonbonded forces can affect the lowest frequencies only since they are too weak to affect the high frequencies. Then our task is to diagonalise the following matrix

$$E_0^T H' E_0 + \Lambda_0, \tag{11}$$

where E_0 and Λ_0 are the matrices of unperturbed eigen vectors and eigen values respectively and H' is the force constant perturbation matrix expressed in mass-weighted Cartesian coordinates for various values of dielectric parameters assigned to the van der Waals interaction and electrostatic interaction. With change in these parameters one of the lowest frequency modes goes to zero value *i.e* the mode softens.

B Exciton–phonon interaction

The concept of phonon assisted reaction can also be extended to photochemical aggregation reaction. In such reaction a strong exciton–phonon coupling may result in the deformation of the lattice near the excited molecule. This deformation can localise excitation. Furthermore, a local conformation which is precursor to the photodimer lattice is created by strong exciton-phonon coupling. This type of reaction is different from defect initiated photoreaction.

The manifestation of strong exciton–phonon coupling in electronic spectra is the lack of fine structure and large Stokes' shift between the absorption and emission maxima or appearance of phonon side bands and line broadening.

Exciton-phonon coupling in molecular crystals and mixed crystals have been discussed by Hochstrasser and Prasad [39,40]. This interaction arises from the variation of excitation exchange interaction and the change in van der Waals interaction with the variation of spatial and orientational coordinates of the molecules in the nonrigid lattice.

The exciton-phonon interaction for molecular crystal under adiabatic approximation can be written as

$$H_{ex}(R) = H_{ex}(R_0) + H_M(R) + H_D(R) \tag{12}$$

Here, R represents the spatial and orientational coordinates of the molecules and $H_{ex}(R_0)$ is the exciton Hamiltonian in the rigid lattice.

$H_M(R)$ depends on excitation exchange interaction between the pairs of molecules and describes the inelastic and elastic scattering of excitons of different wave vectors creating a phonon and conserving total wave vector. This results in the exciton damping creating line broadening of transitions from ground state to the exciton levels.

$H_D(R)$ is a function of the total change in van der Waals interaction between all pairs of molecules when one molecule of the pair is electronically excited. This results in the recoil of molecule in lattice normal coordinate space during electronic transition. The recoil excess energy is in the form of excess potential energy whose dissipation corresponds to lattice relaxation and its magnitude contributes to the "Franck–Condon" factors for phonon sidebands.

When $H_D(R) >> H_M(R)$ the phonon structure is expected to be more prominent *i.e.* the phonon sidebands become more pronounced as the exciton band width becomes smaller. For $H_M(R) >> H_D(R)$, the stationary states are those of delocalised excitons.

Acoustic and optical phonon behave in different ways for exciton-phonon coupling. In general, in a real molecular crystal, the peaks in phonon side bands do not necessarily have to show any correspondence to the peaks in the Raman spectrum. However, the electronic excitation coupling is maximum for zone-center optical phonons. It is therefore, not unlikely that some peaks in phonon side bands have same frequencies as the Raman phonon bands. Also for large density of states and small dispersion of optical phonons, the phonon side bands frequencies may corresponds to the peaks in the Raman spectrum.

The lattice participation in the radiative process in the crystal demands that absorption and emission frequencies are not same in contrast to the free molecular case. The lattice contribution mainly originates from the change of normal coordinates in two electronic states. This frequency shift between electronic absorption and emission is called the Stokes' shift. Large Stokes' shift, therefore, is an indication of strong exciton–phonon coupling.

(*c*) *Concept of reaction cavity :*

Topochemically controlled solid state photoreactions involve minimum atomic or molecular movements which demands the presence of properly juxtaposed reaction centres in the crystals. Again it is believed that in photochemical processes in molecular crystals the structure and orientation of excited states are close to that of ground states. This concept neglects the role of nearest neighbours and the changes due to molecular excitation. Cohen has put forward the concept of 'reaction cavity' which gives due importance to the presence of nearest neighbours [41,42]. This concept is useful to explain variety of solid state reactions and has been extensively used to understand the geometries of excimers of polyaromatics in the crystal [43–46]. The space occupied by the molecule in the crystal is the reaction cavity and the neighbours exert some 'pressure' on the wall of the cavity leading to some distortions which involves a large decrement of attractive forces or large increment of repulsive forces or both. Some restrictions are applied on this distortion by close-packed environment. Those reactions which involve minimum change of the surface of reaction cavity are energetically favoured. This concept is very useful in predicting the product where more than one product is topochemically permitted. The role of molecular environment in the crystal towards

reactivity has been generalised by Gavezzotti [47,48] according to whom the availability of free space around the reaction site is a prerequisite for crystal reactivity.

D Photoinduced lattice instability :

Electronic excitation in a molecular crystal or macromolecular chain may produce a particular type of lattice instability. The electronic excitation may be localized at one lattice site for a time longer than the lattice vibration time scale. The localized excitation then means the existence of an excited molecule which due to its altered properties appears to its neighbours as an impurity. The creation of this impurity molecule introduces a local instability in the lattice configuration which may lead to large molecular displacements. The displacements may in some cases be precursors of the formation of excimers and photochemical reactions. This logic has been put forward by Craig and Collins and found to be valid for one dimensional lattice [49].

For an infinite one-dimensional chain of structureless particles, the typical atom–atom potential can be written as

$$V(r) = D\{[\exp(-B(r - r_{eq})) - 1] - 1\}, \tag{13}$$

where r is the interparticle distance and minimum value of $V(r)$ occurs at $r = r_{eq}$

When one molecule is excited by photon, an impurity is created and the excited molecule interact with its neighbour via the potential $V^*(r)$ given by

$$V^*(r) = D^*\{[\exp(-B^*(r - r^*_{eq})) - 1] - 1\}. \tag{14}$$

Then local instability in the lattice structure is produced. This instability is relieved by large amplitude displacements in more than one possible way. In the simple model one mode leads to new lattice configuration and other yields a metastable nonequilibrium configuration. These two distortions can have significantly different potential energies and both distortions can decrease the potential energy immediately after excitation. Potential energy change is confined to the immediate neighbourhood of excited particle and affects the migration of electronic excitation. Craig and his coworkers [50–52] have cited examples where excimer and exciplexes are formed on excitation in the solid state but not preformed in the ground state. The lattice instability helps to drive one molecule close to its neighbour promoting excimer and exciplex formation. Relaxation of this excimer or exciplex may result in ground state dimer.

3. Apparatus and measurements

X-ray diffraction technique has been widely used to study solid state photoreactions [16,53–55]. But this method is beset with certain drawbacks : (1) It measures space and time averaged structure whereby microscopic details of cluster dynamics are lost. (2) It takes several hours to solve three dimensional structures. (3) X-ray radiation can cause solid state reactions.

Electronic and internal vibrational spectroscopy can be used to identify the products [56] but the reaction dynamics can not be determined from these studies. Electron microscopy has been used by Thomas and his co-workers [57] but its application is limited due to possible radiation damage due to electron beam interaction. In case where reaction involves a single crystal to a single crystal transformation three-wave mixing spectroscopy and laser holography are shown to be promising technique [58].

Laser Raman phonon spectroscopy has recently been introduced as a highly suitable method for studying solid state photoreactions [35,59,60]. It provides informations of both statics and dynamics of reaction. The experimental arrangement is also highly suitable for such studies. The advantages of Raman technique are : (i) An extremely small amount of sample can be used. (ii) No special sample preparation, like making pellet as in infrared or grinding as required in X-ray diffraction, is required. The disadvantages of this technique are : (i) It is not suited for investigations of dilute concentration of species. However, in many cases this can be made possible by resonance enhancement. (ii) It can not be used for any real quantitative study of reaction rate. If reaction rate is not the topic of interest, Raman spectroscopy is indeed a very useful technique for the study of solid state photoreaction.

4. Specific systems

A. Dimerization :

i) p-Chloro cinnamic acid :

p Chloro cinnamic acid (*p*-CCA) crystallizes in the space group $P2_{1/c}$ with four molecules per unit cell [61]. This β-form of the crystal grown from acetic acid solution has the reactive double bond separation 3.87 A which is the distance of *b* axis along which two nearest neighbour molecules are related by mirror symmetry. Solid state photoirradiation gives mirror symmetric 4,4'-dichloro β-truxinic acid as the only product.

Characterization of the reactant and the product has been done by infrared and Raman spectroscopy. The intense aliphatic C=C stretching vibration at 1620 cm^{-1} in the monomer ir spectrum decreases in intensity with reaction progress and finally disappears in the dimer spectrum. This observation in conjunction with the appearance of the cyclobutane ring breathing vibration at 1095 cm^{-1} and the ring deformation vibrations at 672 and 745 cm^{-1} confirms photodimerization by cyclobutane ring formation.

The progress of the reaction was monitored by electronic absorption spectroscopy. Broad absorption bands are observed at 194 nm and 276 nm in the solid film of the monomer. In the dimer spectrum the higher energy band shows a slight red shift while the other band disappears. A new band at 250 nm is also observed in the dimer spectrum.

In the crystalline state *p*-CCA shows strong fluorescence at 300 K. The broad emission band with λ_{max} = 392 nm shifts to higher energy with reaction progress and in the dimer crystal it is observed at 358 nm. As shown in Figure 1, the broad structureless

absorption and emission spectra in the monomer crystal and large Stokes' shift between the two, provide a clear evidence of strong exciton-phonon coupling in the monomer lattice.

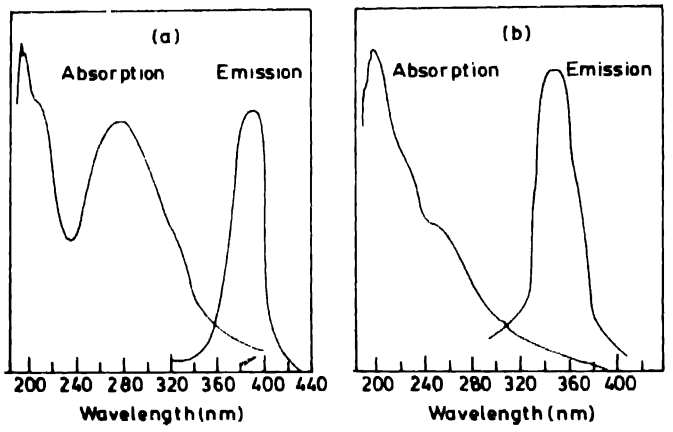

Figure 1. Electronic absorption and emission spectra of (a) monomer and (b) dimer of *p*–CCA in the crystalline state at 300 K (Used by permission, Ref [68])

The Raman phonon spectra of this sample with reaction progress is presented in Figure 2. Six low frequency phonon bands at 11.2, 17.6, 26.0, 36.2, 49.0 and 77 cm $^{-1}$ are observed in the monomer spectrum. With reaction progress these bands suffer a monotonic shift towards lower frequencies. The 11.2 cm $^{-1}$ band disappear in Raleigh wing. On further reaction progress, the bands broaden appreciably. The phonon of extensively photoreacted crystal is weak and diffuse. As no new phonon band appears we can conclude that the product does not form any separate lattice. The nature of the reaction is homogeneous in the initial stages but as the product concentration increases, the lattice becomes progressively disordered.

ii) 2,6 dimethyl p–benzoquinone :

The photoproduct in this crystal depends on the nearest neighbour monomer geometry which controls the interaction of two double bonds >C=C< and >C=O leading to an oxetan or a cage dimer. The quantum yield of the cage dimer is only 0.5% [62].

Intramolecular vibrations observed in infra-red and Raman spectra were exploited to get information about the photoproduct. The observation of the two infra–red bands at 1676 cm $^{-1}$ and 1634 cm^{-1} both in the photoproduct and in the oxetan dimer and disappearance of C=O stretching band at 1668 cm^{-1} in the monomer crystal on photodimerization point to that oxetan is the primary photoproduct of 2,6 dimethyl benzoquinone crystal. Absence of any band at 1715 cm^{-1} or 1700 cm^{-1} in the IR spectrum of partially dimerized crystal also confirms the above conclusion.

From the phonon spectra as a function of reaction progress it is found that the monomer bands at 55, 62, 67, 71, 75 and 88 cm $^{-1}$ show significant shift on dimerization.

Two new bands appear at 47 and 60 cm^{-1} which gain in intensity with reaction progress and finally broad band having a little structure and covering a wide spectral range is observed. This suggests that in the initial stage reaction mechanism is homogeneous due to the fact that at low concentration the product form solid solution in the monomer lattice but as the reaction proceeds the product segregates out and forms its own lattice.

Electronic absorption spectra of 2,6 dimethyl *p*-benzoquinone at 6 K is shown in Figure 3. A zero phonon transition at 19952 cm^{-1} is observed with prominent phonon side bands which fit into a progression of 65 cm^{-1} phonon. This may correspond to one of the

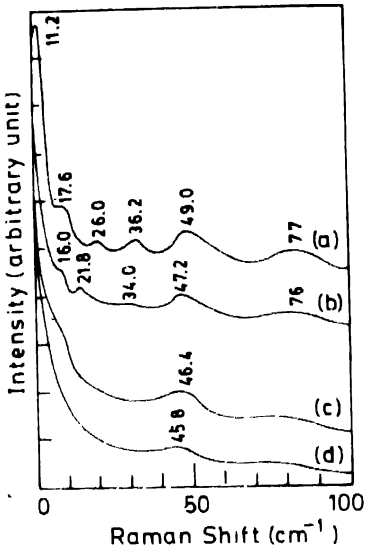

Figure 2. The Raman phonon spectra of *p*-CCA crystal with reaction progress at 300 K (a–d in the increasing order of dimerization) (Used by permission, Ref [68])

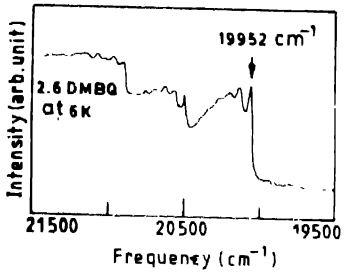

Figure 3. Electronic absorption spectra of 2,6 dimethyl *p*-benzoquinone crystal at 6 K (Used by permission, Ref. [59])

observed phonon bands at 62 and 67 cm^{-1} in the Raman spectrum. It appears that the exciton-phonon coupling is selective and occurs with this specific phonon mode. These observations indicate that in this reaction, strong exciton-phonon coupling with a specific phonon mode results in the formation of polaron. This provides a local conformational change in the lattice which is a precursor to the photoproduct lattice.

iii) 7–methoxy coumarin :

7–methoxy coumarin (7–MC) is a typical member of the family where apparent violation of Schmidt's topochemical criteria is observed. According to X–ray crystallographic study [63] the reactive double bonds of two nearest neighbour 7–MC molecules in the lattice are rotated by 65° with respect to each other and centre-centre distance of reactive double bonds is 3.88 A. The formation of only solid state photoproduct, the symmetrical head–tail dimer, was explained by Murthy *et al*[64] who postulated an inherent flexibility in the monomer crystal

for the molecules to undergo rotation. They also ruled out defects as the possible loci for reaction from percentage yield versus time plot.

We have used infra-red and Raman spectroscopy for characterization of reactant and product. The disappearance of C=C stretching vibration at 1556 cm $^{-1}$ of pyrone moiety in the dimer spectrum indicates that the double bonds between C(3) and C(4) are used to form cyclobutane ring. Appearance of cyclobutane ring breathing vibration at 1016 cm $^{-1}$ and ring deformation and bending modes at 719 and 590 cm $^{-1}$ respectively add further evidence of the cyclobutane ring formation. The C=O stretching vibration at 1716 cm $^{-1}$ is lower than free lactone carbonyl frequency (1725 cm $^{-1}$) which is due to greater single bond character of the more polar carbonyl group in presence of the aromatic structure. This mode shifts to 1747 cm $^{-1}$ on dimerization resulting from the loss of conjugation.

The blue shift of the broad absorption band with λ_{max} = 354 nm with dimerization is a general observation and attributed to the loss of conjugation. The strong fluorescence spectra even at room temperature with λ_{max} at 391 nm is due to absence of intersystem crossing $^1\pi\pi^* \rightarrow {}^3\pi\pi^*$ since $^1\pi\pi^*$ is significantly lowered form $^3\pi\pi^*$ state in the crystal state. The emission band shifts to higher energy on dimerization. Considerable overlap between emission and absorption spectra as shown in Figure 4 suggests that exciton-phonon coupling is rather weak in this crystal.

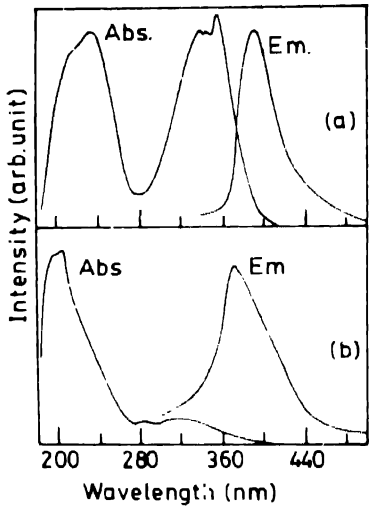

Figure 4. Electronic absorption and emission spectra of (a) monomer and (b) dimer of 7-MC in solid film at 300 K. (Used by permission, Ref [38])

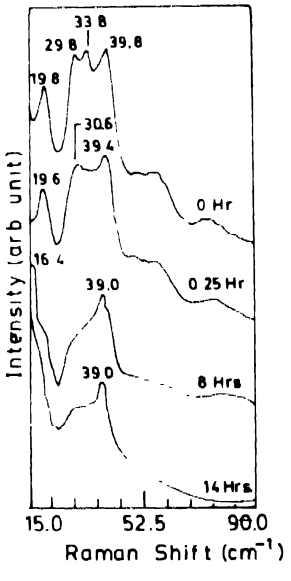

Figure 5. Raman phonon spectra of 7-MC crystal with reaction progress at 300 K. (Used by permission, Ref [38])

7-MC crystal grown from benzene solution belongs to the space group P1 with four molecules per unit cell which demands that six A_g phonons should be Raman active. Figure 5

shows that the monomer crystal is characterised by four sharp and moderately intense low frequency phonons at 19.8, 29.8, 33.8 and 39.8 cm^{-1} in addition to weak broad bands at 52.5 and 74.2 cm^{-1}. As the reaction proceeds, except the 19.8 cm^{-1} band, all the other phonon bands broaden appreciably and no significant shift in frequency is observed. The 19.8 cm^{-1} band gradually shifts to lower frequency on reaction progress and finally disappears in the Releigh wing. The appearance of no new phonon band and the softening of 19.8 cm^{-1} band suggest that the photoreaction is assisted by softening of this phonon mode.

In the monomer crystal the reactive pair may undergo librational motion about the minor axes L_1 and L_2 which are nearly in the plane of coumarin ring and about the major axis L_3 perpendicular to the ring [65]. A part of energy from the radiation field is used to increase the thermal energy of the system which increases the librational motion. The 19.8 cm^{-1} band is likely to arise from librational motion of monomer molecules around L_3 axis and this may bring the reactive double bonds of the molecular pair in a favourable configuration for the reaction to occur.

According to the concept of 'dynamic preformation' [49-52] of photoproduct, the motion of electronically excited molecules towards maximum overlap geometry would involve less energy than that for the ground state molecules. It is possible that softening of a phonon mode may come about through such a process.

B Polymerization .

i) Dimethyl ester of α,α´ dicyano p–phenylene diacrylic acid .

The sample is a member of α,α´ dicyano *p*–phenylene diacrylic acid (*p*–CPA) series which structurally is an extension of α–cyano cinnamic acid molecule. These samples contain two unsaturated centres and four centre type polymerization occurs on photoirradiation.

The photopolymerization is by cyclobutane ring formation as evidenced by disappearance of C=C stretching mode and HC=CH trans vibration in the polymer spectrum. The cyclobutane ring breathing vibration at 1000 cm^{-1} in the polymer spectrum also supports the above conclusion. The C=O stretching mode in monomer at 1757 cm^{-1} shifts to 1763 cm^{-1} in the polymer. This small shift can be attributed to the fact that the resulting polymer is not of high molecular weight as cis–trans isomerization may occur during polymerization [66].

The electronic excitation and emission spectra of monomer and polymer are shown in Figure 6. The monomer emission peaks are at 462 and 497 nm. The excitation peaks are at 363 and 394 nm. Since the large Stoke's shift is a clear indication of exciton–phonon coupling caused by strong lattice distortion in the excited state the photoreaction is likely to be phonon mediated. The polymer emission bands are at 382, 407 and 450 nm. The excitation spectra shows two peaks at 361 and 379 nm. In the polymer exciton-phonon coupling is rather weak as suggested by considerable overlap between excitation and emission spectra.

Figure 7 shows Raman phonon spectra with reaction progress. At room temperature there are four distinct bands at 33.2, 57.8, 78.4 and 128.8 cm $^{-1}$ in the monomer. With reaction progress the intensity of the bands decrease and the bands shift towards higher wavenumbers. After 6 h irradiation only two phonon bands persist at 37.0 and 65.0 cm^{-1} which are shifted from their initial positions by 3.8 and 6.2 cm $^{-1}$ respectively. Progressive broadening of phonon spectra suggest increasing lattice disorder and amorphous nature of the polymer is confirmed by the absence of any phonon bands after 14 h of irradiation. So the reaction mechanism is homogeneous in the initial stages and the lattice becomes disordered with increasing photoproduct concentration.

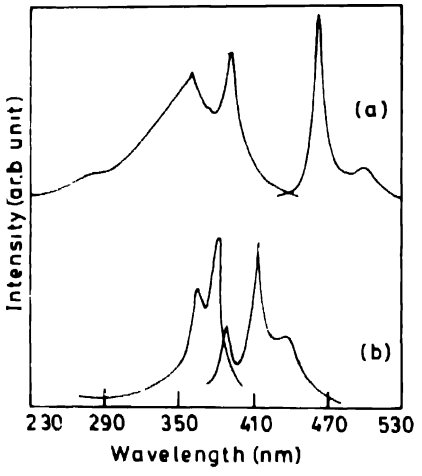

Figure 6. Electronic excitation and emission spectra of (a) monomer and (b) polymer of *p*-CPAMe at 77 K (Used by permission, Ref [69])

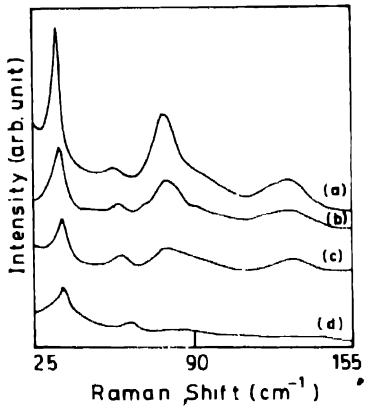

Figure 7. Raman phonon spectra of *p*-CPAMe polycrystals with reaction progress a–d are in the increasing order of reaction (Exposed for a 0 min, b 120 min, c 240 min., d 360 min). (Used by permission, Ref. [69]).

ii) Di n-propyl ester of α,α′ dicyano p-phenylene diacrylic acid :

It is the most reactive member of *p*-CPA series. In this crystal, the separation between reactive double bonds is 3.931 A [67]. This sample on photoirradiation has been found to polymerize into a linear, high molecular weight crystalline polymer containing cyclobutane ring in the main chain.

The infra-red spectra show that the aliphatic C=C stretching vibration at 1603 cm^{-1} and trans HC=CH vibration at 969 cm $^{-1}$ decrease in intensity with reaction progress and in extensively reacted crystal these bands disappear. The cyclobutane ring formation and four-centre type photopolymerization is thus confirmed. The C=O stretching mode at 1720 cm $^{-1}$ in monomer shifts to 1736 cm $^{-1}$ on polymerization due to loss of conjugation which suggests high molecular weight polymer formation in contrast to dimethyl ester of *p*-CPA where this shift is only 6 cm^{-1}.

The monomer is strongly fluorescent in the crystalline state. No phosphorescence emission is observed. As shown in Figure 8 the excitation and emission maxima are separated and their separation is smaller than that in dimethyl ester of *p*–CPA. So here exciton-phonon coupling is present though it is not as strong as in the dimethyl ester crystal. As the reaction proceeds, the emission and excitation peaks are shifted towards high energy side and in the polymer spectra considerable overlap between emission and excitation spectra suggests a rather weak exciton-phonon coupling in the polymer lattice.

The evolution of Raman phonon spectra with reaction progress is shown in Figure 9. The monomer spectrum shows seven bands at 23.4, 32.2, 51.6, 86.6, 103.0, 136.8 and 162 cm^{-1}. With reaction progress the bands show slight shift towards lower frequency and

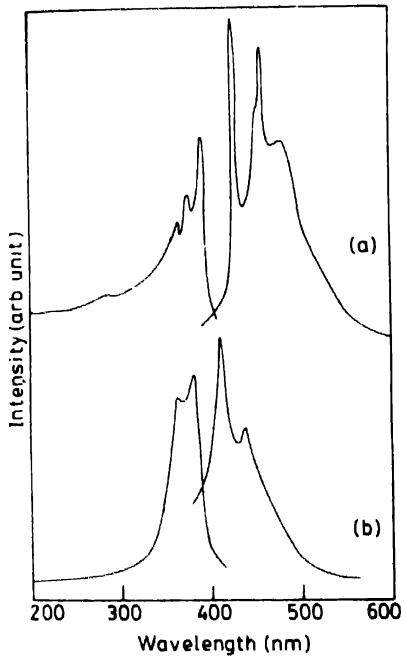

Figure 8. Electronic excitation and emission spectra of (a) monomer and (b) polymer of *p*–CPA nPr at 77 K

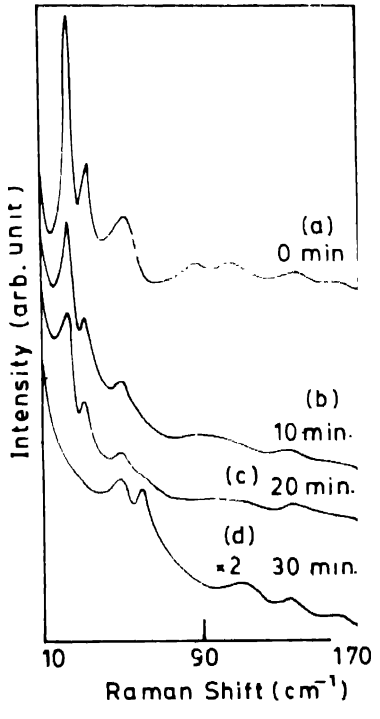

Figure 9. Raman phonon spectra of *p*–CPA nPr polycrystals with reaction progress a–d are in the increasing order of reaction. (Exposed for a 0 min., b . 10 min., c · 20 min , d . 30 min)

after 20 minutes irradiation, the monomer bands at 23.4 and 32.2 cm^{-1} shift to 22.4 and 30.8 cm^{-1} respectively. So the reaction mechanism is homogeneous in the initial stages and the reactant and product form solid solution. At this stage, a new phonon band at 59.8 cm^{-1} starts developing and the 86.6 and 103.0 cm^{-1} bands are broadened. On further reaction progress the 59.8 cm^{-1} phonon gains intensity and another band at 111.6 cm^{-1} appears. The monomer phonon modes at 23.4 and 32.2 cm^{-1} gradually loose their intensity and disappear in the

polymer spectrum. These results suggest that the reaction mechanism is heterogeneous in the final stages and the phase separation between the reactant and the product occurs. Sharpening of the phonon bands to some extent in the polymer spectrum suggests good degree of order in the polymer lattice. We conclude that the photoreaction in this crystal is mediated by phonon through strong exciton-phonon coupling.

iii) Diethyl ester of p- phenylene diacrylic acid :

Ethanol grown monomer crystal belongs to the space group $P2_1/a$ with reacting double bond separation 3.970 A [67]. The photoproduct is a high molecular weight polycrystalline powder.

The aliphatic >C=C< stretching mode at 1640 cm $^{-1}$ and trans HC=CH vibration at 1000 cm $^{-1}$ are intense in the monomer spectrum and disappears in the extensively reacted crystal. These suggest the formation of cyclobutane ring. Also a cyclobutane ring breathing at 1040 cm $^{-1}$ and other ring vibrations appear in the infrared spectrum of the photoreacted crystal. There is a 20 cm $^{-1}$ shift of C=O stretching mode on polymerization which points to the high molecular weight of the polymer.

The emission and excitation spectra of the monomer and the polymer crystal at 77 K are shown in Figure 10. It is observed that the emission spectrum of the monomer is well structured with (0,0) band at 362 nm and strong vibrational peaks. The exciton-phonon

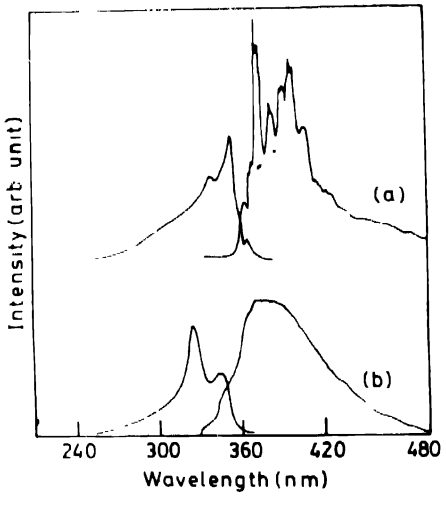

Figure 10 Electronic excitation and emission spectra of (a) monomer and (b) polymer of *p*-PDAEt at 77 K (Used by permission, Ref [69])

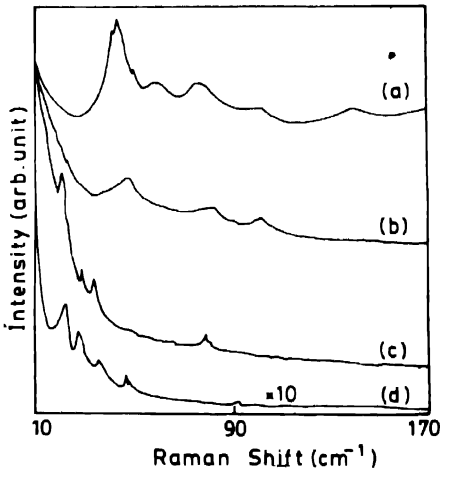

Figure 11. Raman phonon spectra of *p*-PDAEt polycrystals with reaction progress. a–d are in the increasing order of reaction. (Exposed for a : 0 min , b 60 min , c · 120 min., d · 180 min.). (Used by permission, Ref [69]).

coupling is weak in the monomer lattice as evidenced from the appearance of fine structures in the emission spectrum and overlapping between emission and excitation spectra. So the lattice phonon is unlikely to play any significant role in this polymerization reaction.

The Raman phonon spectra at different reaction stages are shown in Figure 11. In the initial stages disorder in the lattice with formation of lower-order polymers is manifested in broadening of phonon modes.Frequency shifts in the initial stages also points to the homogeneous nature of initial reaction mechanism. In the later stage, however, new sharp bands appear due to phase separation between the reactant and the product. Though of poor intensity, the sharp phonon bands suggest that the polymer lattice is highly ordered. On further reaction progress, the sharp structure of phonon spectrum persists indicating that the ordered structure of the lattice is retained. The phonon frequencies, however, show a monotonic shift to higher values. This indicates that on further reaction, still higher order polymers are formed. This product is formed in a homogeneous mechanism keeping the high degree of order in the lattice.

5. Conclusion

This article focuses on the novelty of phonon probe in deriving the dynamic concept of reactivity and the mechanism of solid state photoreactions. Phonon participation in such reactions may occur through strong exciton-phonon coupling or through a mode softening. The strength of exciton-phonon coupling is different for different systems. In some reactions lattice phonon do not influence reactivity significantly. The reaction mechanism may be homogeneous or heterogeneous. In the former the reactant and the product form solid solution whereas in the latter the reactant and the product form separate lattices. In many cases mixed behaviour is also observed.

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2. Electronic spectroscopy of organic molecules & molecular crystals : Exciton Splitting, exciton–exciton interaction, triplet exciton dynamics.

3. Vibrational spectroscopy and molecular geometry elucidation.
4. Charge carrier generation and transport in organic conductors, semiconductors and photoconductors.
5. Organic material based device development : Solid state batteries, photovolatic cells, gas sensors and biosensors.
6 Organised molecular assembles and ultra-thin Langmuir–Blodgett molecular films : Charge transport and energy transport

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